Japanese Patent Laid-Open No. 63794/1983 (58-063794)

Laid-Open Date: April 15, 1983

Request for Examination: Not made

Application No.: 162159/1981

Application Date: October 12, 1981

Inventors: Yoshikazu Shoji et al.

Applicant: Asahi Denka Kogyo K.K.

Specification

1. Title of the Invention

Aqueous Lubricating Compositions

2. Claim

An aqueous lubricating composition comprising 0.05 - 30 wt% of a compound of the general formula:

$$\left[\begin{array}{c} R_1 \\ R_2 \end{array}\right] \text{NCS}_2 Mo_2 \text{SxOy} \tag{1}$$

(wherein R_1 and R_2 represent a hydrocarbon group of 1-18 carbon atoms which may be substituted by a hydroxy group or alkoxy group, and R_1 and R_2 may be the same or different; x and y are respectively a number of 0 to 4, and x+y=4).

3. Detailed Description of the Invention

The present invention relates to aqueous lubricating compositions.

The aqueous lubricating compositions have drawn attention to their fireproof. In particular, recently, the

highly hydrous type of hydraulic liquid containing much water has been watched in view of saving of resources and the protection of the environment. Further, the aqueous lubricating compositions have frequently been employed in press oil, cutting fluid, and the like.

The aqueous lubricating compositions, however, are difficult to exhibit extreme pressure and lubricity, and appearance of a better extreme pressure additive has been desired, accordingly.

The purpose of the invention is to provide a highly lubricant aqueous lubricating composition with no defect as mentioned above using an organomolybdenum compound.

The composition of the invention comprises a large quantity of water and 0.05 to 30 wt% of a compound of the general formula:

$${ \left[\begin{array}{c} R_1 \\ R_2 \end{array} \right]} NCS_2 MO_2 SXOY \tag{1}$$

(wherein R_1 and R_2 represent a hydrocarbon group of 1-18 carbon atoms which may be substituted by a hydroxy group or alkoxy group, and R_1 and R_2 may be the same or different; x and y are respectively a number of 0 to 4, and x+y=4) as essential components.

The compounds of the general formula (I) are known and can be obtained, for example, according to the method as described in Japanese Patent Publication Nos. 24562/1970 and

31646/1978.

The compounds of the general formula (I) to be added are effective in a content of 0.05wt% or more, but the effect is not so increased by addition of large quantities. Therefore, the compounds may be used in an amount up to 30wt% as limitation, and in general the amount of approximately 0.1 to 5wt% is preferred.

Since the compounds of the general formula (I) usually is not soluble in water, they may be dispersed or solubilized with a dispersing agent or solubilizing agent in using.

The dispersing agent or solubilizing agent may be chosen properly. In view of the stability with a lapse of day, however, it is preferred to use a method for emulsifying or solubilizing the compounds into a polyhydroxy compound or its aqueous solution in the presence of a protein, protein lysate and/or a surface activator.

In such a case, the above protein to be used includes water-soluble proteins, e.g., casein sodium, soybean protein, nonfat milk, whey powder, raw egg white, dry egg white, blood powder, meat powder, microorganism protein, peptone, yeast extract, albumin, lactoalbumin, globulin, lactoglobulin, glutelin, protamine, histamine, and the like. As the above protein lysate, those derived from the above proteins by decomposition with protease may be used.

As the above-described surface activator, a variety of

surfactants including anion type, non-ionic type, cation type, and amphoteric type may be used. The anionic surface activator includes carboxylic acid salts, e.g., soap, N-acylamino acid salts, alkyl ether carboxylic acids, acylated peptides, etc.; alkylsulfonic e.g., salts, sulfonic acid alkylbenzenesulfonic acid salts, alkylnaphthalene sulfonic their formalin condensates, salts and dialkylsulfosuccinic acid esters salts, α -olefinsulfonic acids, N-acylmethyl-taurines, etc.; sulfuric acid ester salts, e.g., sulfated oil, alkylsulfate salts, alkyl ether sulfate salts, alkyl allyl ether sulfate salts, alkylamide sulfate salts, etc.; and phosphoric acid ester salts, alkylphosphate salts, alkyl ether phosphate salts, alkyl allyl ether phosphate salts, etc. The non-ionic surface activator includes ether type activators, e.g., polyoxyethylene alkyl secondary alcohol polyoxyethylene polyoxyethylene alkylphenyl ether, oxyethylene derivatives of polyoxyethylene condensate, alkylphenol formalin polyoxypropylene block polymer, etc.; ether ester type activators, e.g., polyoxyethylene glycerin fatty acid esters, polyoxy-ethylene castor oil and hardened castor oil, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, etc.; ester type activators, e.g., polyoxyethylene glycol fatty acid esters, fatty acid monoglycerides, sorbitan fatty acid esters, sucrose fatty acid

esters, etc.; and nitrogen-containing type activators, e.g., fatty acid alkanol amides, polyoxyethylene fatty acid amides, polyoxyethylene alkylamines, alkylamine oxides, etc. Further, the cation type activator includes, for example, alkylamine quaternary ammonium salts, benzalkonium salts, benbitonium chloride, pyridinium salts, and the like. example, surface activator includes, amphoteric carboxybetaine type, sulfo-betaine type, aminocarboxylic acid satls, imidazolinium betaine, lecithin, and the like. addition, fluorine type surfactants and silicone type surfactants may also be used.

In the above-described emulsifying or solubilizing method, the above-described surface activator may not be used necessarily, and it is preferred to use a material selected from proteins such as casein sodium or protein lysates.

As the above-described polyhydroxy compounds, for example, dihydric alcohols such as propylene glycol, trihydric alcohols such as glycerin, sugar alcohols such as sorbitol, mannitol, etc., monosaccharides such as glucose, fructose, etc., di- or tri- or higher oligo-saccharides such as sucrose, maltose, galactose, etc., a variety of invert sugars obtained by hydrolysis of starch, starch syrup, dextrin, isomerized sugars, syrup, honey, jams, and the like may be used. The liquid polyhydroxy compound includes those that are liquid at usual temperature and selected from the above-described

polyhydroxy compounds, including, for example, propylene glycol, glycerin, and the like.

The rate of the above-described respective components used in emulsification or solubilization of the compounds of the formula (I) is 0.005% or more (by weight, hereinafter the same), preferably 0.05% or more, particularly 0.05-5%, for the sum of one or more members selected from the group consisting of proteins, protein lysates and surface activators, and a polyhydroxy compound or water, wherein the rate of the polyhydroxy compound for the sum is 30% or more, preferably 40%. For example, when a liquid polyhydroxy compound is used, it may be used in an amount of nearly 100%.

When the organomolybdenum compound of the above formula (I), which has high melting point and is hardly emulsified or solubilized, is intended to be emulsified or solubilized according to the above method, the compound may be dissolved in a proper solvent to emulsify or solubilize. In such a case, it is possible to use a solvent which has no compatibility with the hydroxy compounds, for example, chlorinated or ester-type solvents such as dioctyl phthalate, diisodecyl adipate, dioctyl adipate, chlorinated paraffin, chlorinated fatty acids, and the like.

To the above-described organomolybdenum compound or its solubilized compound in a solvent may be added a protein (lysate), a surface activator, and a polyhydroxy compound or

water to give an emulsified or solubilized organomolybdenum compound, which is mixed with water to give the composition of the invention.

The mixing ratio of the emulsifying or solubilizing agent containing the above protein to the organo-molybdenum compound or its mixture with a solvent is fixed in 1 part of the former to 4 parts or less of the latter (ratio by weight). As far as gel is not formed, the amount of the latter may be increased.

In the component of the invention, as far as the effect of the invention is not spoiled, the followings may optionally be added. Thickener, for example, cellulose type, gum type, chitosan type, alginic acid type, their alkali metal salts, ethoxy derivatives, polyoxyalkylene ester derivatives, polyols from amines and polyols, etc., e.g., beef tallow amine, cyclohexyl amine ethoxy derivatives, polyoxyalkylene glycols or their urethane denaturated derivatives, and the like. Rust amines, carboxylic acids, and the preventives: Corrosion inhibitors: benzotriazole, meracptobenzo-triazole, mercaptobenzothiazole, and the like. Defoaming agents: silicone type, alcohol type, and the like. Coloring agents. Water softening agents. (EDTA, etc.) Or extreme pressure agents other than the above-described compounds of the formula (I), for example, chlorinated paraffin, chlorinated fatty acids, fat and oil sulfides, ester sulfides, olefin sulfides, phosphates, phosphites, metal dithiocarbamates (zinc, iron,

copper, etc.), dialkyl (or allyl) dithiophosphoric acid salt phosphonates, phosphinates, and the like.

The invention will be explained by the following examples.

Preparation 1

Under heating, 2.5 parts (by weight part, hereinafter the same) of casein sodium and 97.5 parts of glycerin were mixed. To this mixture was added a solution of 20 parts of

$$[(C_8H_{17})_2NCS_2]_2-MO_2S_2O_2$$

dissolved in 80 parts of dioctyl phthalate under stirring to give a water-emulsifiable or solubilizable composition. This is called Composition (A).

Preparation 2

Under heating, 5 parts of sodium dodecyl-benzenesulfonate, 10 parts of propylene glycol and 85 parts of glycerin were mixed. To this mixture was added a solution of 30 parts of

$$[(C_8H_{17})_2NCS_2]_2MO_2S_{1.5}O_{2.5}$$

dissolved in 70 parts of chlorinated paraffin CB-419 (Asahi Denka Kogyo K.K.) under stirring to give a water-emulsifiable or solubilizable composition. This is called Composition (B). Preparation 3

A mixture of 10 parts of $[(C_8H_{17})_2NCS_2]_2Mo_2S_{2.1}O_{1.9}$, 40 parts of dioctyl phthalate, 49 parts of glycerin, and 1 part of sodium dodecylbenzenesulfonate (2.5% aqueous solution) was stirred

vigorously to give a composition. This is called Composition (C).

Preparation 4

A mixture of 5 parts of $[(C_4H_9)_2NCS_2]_2Mo_2S_{1.5}O_{2.5}$, 45 parts of dibutyl phthalate, 5 parts of nonylphenol ethoxylate (the added EO, 10 moles, 5% aqueous solution), and 45 parts of propylene glycol was stirred vigorously to give a composition. This is called Composition (D).

Preparation 5

As an organomolybdenum compound, 10 parts of $[(C_{12}H_{25})_2NCS_2]_2Mo_2S_3O_1$ was used. Otherwise, a composition was prepared in the same manner as in Example 3. This is called Composition (E).

Preparation 6

A mixture of 10 parts of $[(C_{18}H_{37})_2NCS_2]_2Mo_2S_1O_3$, 10 parts of zinc di-sec-hexyldithiophosphate, 30 parts of dioctyl diadipate, 48 parts of glycerin, and 2 parts of sodium dodecylbenzenesulfonate (2.5% aqueous solution) was stirred vigorously to give a composition. This is called Composition (F).

Preparation 7

In place of the organomolybdenum compound used in Preparation 3, $[(C_5H_{11})_2NCS_2]_2Sb$ was used. Otherwise, a composition was prepared in the same manner as in Preparation 3. This is called Composition (x).

Example

Using Compositions (A), (B), (C), (D), (E), (F) and (x) prepared in Preparations 1 - 7 as described above, those compositions were mixed with the respective components as shown in Table 1 below to give the aqueous hydraulic oils (a), (b), (c), (d), (e), (f) and (g). These aqueous hydraulic oils were subjected to a shell 4 balls test (1500 rpm, 20 Kg/cm², wear flaws were measured after a lapse of 15 minutes) and a vane pump test (using a Vickers vane pump V-105C, the wear rate of the vane and the cam ring was measured after a lapse of 50 hours at a discharge pressure 50 Kg/cm², shaft revolution number 1200 rpm, liquid temperature 40°C). Table 2 shows the results.

Table 1

Composition Aqueous hydraulic oils	(a)	(b)	(c)	(d)	(e)	(f)	(g)
Composition (A)	-3						
" (B)		2					
" (C)			3				
" (D)				5			
" (E)					3	}	
" (F)						2	
" (x)				<u> </u>			3
Thickener Extreme pressure of phosphorus type	1	1 0. 5	· 1	1	1	1	1
Rust preventive & Anti-oxidant	2	2	2	2	2	2	2
Distilled water	94	94. 5	94	92	94	95	94

Table 2

Aquous hydraulic oil	Shell 4-balls test wear (mg)	Pump test Vane wear (mg)	Pump test Cam ring wear (mg)
(a)	0. 401	7	640
(b)	0. 381	4	530
(c)	0. 392	8	780
(d)	0. 432	9	630
(e)	0. 445	12	650
(f)	0. 375	. 8	525
(g)	0. 513	30	1050